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(54) Well cement compositions

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(73) Proprietor: **Halliburton Energy Services, Inc.**
Duncan, Oklahoma 73536 (US)

(72) Inventors:
• **Chatterji, Jiten**
Duncan, Oklahoma 73533 (US)
• **Totten, Patty L.**
Duncan, Oklahoma 73533 (US)
• **King, Bobby J.**
Duncan, Oklahoma 73533 (US)
• **Onan, David D.**
Lawton, Oklahoma 73537 (US)

(74) Representative: **Wain, Christopher Paul et al**
A.A. Thornton & Co.
235 High Holborn
London WC1V 7LE (GB)

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- **SMITH T ET AL: "LIGHT, STRONG FOAMED CEMENT: A NEW TOOL FOR PROBLEM WELLS" WORLD OIL, vol. 198, no. 6, May 1984, pages 135-144, XP002024854**
- **CHEMICAL ABSTRACTS, vol. 108, no. 20, 16 May 1988 Columbus, Ohio, US; abstract no. 172515m, SUZUKI, KIICHI: "Fire-resistant lightweight building materials" page 324; XP000157497 & JP 63 017 273 A**

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Description

[0001] The present invention relates generally to the cementing of subterranean wells and, more particularly, to cement compositions which set downhole into resilient solid masses.

[0002] Hydraulic cement compositions are commonly utilized in subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby pipes such as casings and liners are cemented in well bores. In performing primary cementing, a hydraulic cement composition is pumped into the annular space between the walls of the well bore and the exterior surfaces of pipe disposed therein. The cement composition is permitted to set in the annular space thereby forming an annular sheath of hardened substantially impermeable cement therein. The cement sheath physically supports and positions the pipe in the well bore and bonds the exterior surfaces of the pipe to the walls of the well bore whereby the undesirable migration of fluids between zones or formations penetrated by the well bore is prevented. The cement compositions utilized in primary cementing must often be lightweight to prevent excessive hydrostatic pressures from being exerted on formations penetrated by well bores.

[0003] The transition time of a well cement composition is the time after its placement in a subterranean zone penetrated by a well bore during which the cement composition changes from a true fluid to a hard set mass. During the transition time, the cement composition becomes partially self-supporting which lowers the hydrostatic pressure exerted by the cement composition on formations containing pressurized fluid penetrated by the well bore. That is, when the cement composition becomes partially self-supporting, volume reductions in the cement composition caused by fluid loss to adjacent formations and hydration of the cement result in rapid decreases in the hydrostatic pressure exerted by the cement composition. When the fluid phase within the cement matrix is not compressible and the pressure exerted by the cement composition falls below the pressure of formation fluids, the formation fluids enter the annulus and flow through the cement composition forming undesirable flow passages which remain after the cement composition sets. The use of a highly compressible fluid component, like gas, in the cement composition improves the composition's ability to maintain pressure and thus prevents the flow of formation fluids into and/or through the cement composition.

[0004] The development of wells including one or more laterals to increase production has recently taken place. Such multi-lateral wells include vertical or deviated (including horizontal) principal well bores having one or more ancillary laterally extending well bores connected thereto. Drilling and completion equipment has been developed which allows multiple laterals to be drilled from a principal cased and cemented well bore. Each of the lateral well bores can include a liner cemented therein which is tied into the principal well bore. The lateral well bores can be vertical or deviated and can be drilled into predetermined producing formations or zones at any time in the productive life cycle of the well.

[0005] In both conventional single bore wells and multi-lateral wells having several bores, the cement composition utilized for cementing casing or liners in the well bores must develop high bond strength after setting and also have sufficient resiliency, i.e., elasticity and ductility, to resist loss of pipe or formation bond, cracking and/or shattering as a result of pipe movement, impacts and/or shocks subsequently generated by drilling and other well operations. The bond loss, cracking and/or shattering of the set cement allows leakage of formation fluids through at least portions of the well bore or bores which can be highly detrimental.

[0006] Set cement in wells, and particularly the set cement forming the cement sheaths in the annuli between pipes and the walls of well bores, often fail due to shear and compressional stresses exerted on the set cement. Such stress conditions are commonly the result of relatively high fluid pressures and/or temperatures inside pipe cemented in well bores during testing, perforating, fluid injection and/or fluid production. The high internal pipe pressure and/or temperature results in expansion of the pipe, both radially and longitudinally, which places stresses on the cement sheath causing it to crack or the bonds between the exterior surfaces of the pipe and/or the well bore walls and the cement sheath to fail in the form of loss of hydraulic seal.

[0007] Another condition results from exceedingly high pressures which occur inside the cement sheath due to the thermal expansion of fluids trapped within the cement sheath. This condition often occurs as a result of high temperature differentials created during the injection or production of high temperature fluids through the well bore, e.g., wells subjected to steam recovery or the production of hot formation fluids from high temperature formations. Typically, the pressure of the trapped fluids exceeds the collapse pressure of the cement and pipe causing leaks and bond failure. Yet another compressional stress condition occurs as a result of outside forces exerted on the cement sheath due to formation shifting and overburden pressures.

[0008] In multi-lateral wells wherein pipe has been cemented in well bores using conventional well cement slurries which set into brittle solid masses, the brittle set cement cannot withstand impacts and shocks subsequently generated by drilling and other well operations carried out in the multiple laterals without cracking or shattering.

[0009] The above described failures can result in loss of production, environmental pollution, hazardous rig operations and/or hazardous production operations. The most common hazard is the presence of gas pressure at the well head.

[0010] Thus, there are needs for well cement compositions and methods whereby after setting the cement compositions are highly resilient and can withstand the above described stresses without failure. That is, there is a need for well cement compositions and methods whereby the set cement has improved mechanical properties including elasticity and ductility and failures due to pipe movement, impacts and shocks are reduced or prevented.

[0011] We have now devised a resilient well cement composition which has improved mechanical properties including elasticity and ductility, to meet or go towards meeting the needs described above and to overcome or mitigate the deficiencies of the prior art.

[0012] According to the present invention, there is provided a well cement composition having improved mechanical properties including elasticity and ductility, the composition comprising a hydraulic cement; an aqueous rubber latex present in an amount of from 2.5% to 45% by weight of hydraulic cement in said composition; a latex stabilizer; a defoaming agent comprised of polydimethylsiloxane present in an amount of from 0.1% to 0.9% by weight of cement in said composition; a gas present in an amount sufficient to foam said cement composition and produce a cement composition density in the range of 0,96 to 1,91 kg/dm³ (from 8 to 16 pounds per U.S. gallon); a foaming agent; and a foam stabilizer.

[0013] The well cement compositions of the invention are useful in a variety of well completion and remedial operations. They are particularly useful in primary cementing, i.e. cementing casings and liners in well bores including the cementing of multi-lateral subterranean wells.

[0014] A variety of hydraulic cements can be utilized in accordance with the present invention including those comprised of calcium, aluminum, silicon, oxygen and/or sulfur which set and harden by reaction with water. Such hydraulic cements include Portland cements, pozzolana cements, gypsum cements, high aluminium content cements, silica cements and high alkalinity cements. Portland cements are generally preferred for use in accordance with the present invention. Portland cements of the types defined and described in API Specification For Materials And Testing For Well Cements, API Specification 10, 5th Edition, dated July 1, 1990 of the American Petroleum Institute are particularly suitable. Preferred API Portland cements include classes A, B, C, G and H, with API classes G and H being more preferred and class G being the most preferred.

[0015] The compositions of the invention may be free of fumed silica or they may contain fumed silica. Fumed silica is a colloidal form of silica made by the combustion of silicone tetrachloride in hydrogen-oxygen furnaces. Fumed silica is of a fine particle size, and in combination with the other components of the cement compositions of this invention provides improved mechanical properties to the compositions, particularly the ability to withstand a wide range of stresses associated with subterranean well conditions without bond loss, cracking, shattering or other form of failure. The term "fumed silica" is used herein to mean the fumed silica made as described above and equivalent forms of silica made in other ways.

[0016] The fumed silica is present in the above described composition of this invention in an amount in the range of from about 5% to about 30% by weight of the hydraulic cement in the composition (from about 2,04 to about 13,6 kg/sack (4.5 to about 30 lb/sack)), more preferably from about 7.5% to about 15% (from about 3,2 to about 6,4 kg/sack (7 to about 14 lb/sack)) and most preferably about 10% (about 4,3 kg/sack (9.4 lb/sack)). As will be understood by those skilled in the art, the fumed silica reacts with lime liberated by the hydraulic cement during hydration to form an amorphous metal silicate hydrate.

[0017] A variety of well known rubber material can be utilized in accordance with the present invention. Such materials are commercially available in aqueous latex form, i.e. aqueous dispersions or emulsions. For example, natural rubber (cis-1,4-polyisoprene) and most of its modified types can be utilized. Synthetic polymers of various types can also be used including styrene/butadiene rubber, cis-1,4-polybutadiene rubber and blends thereof with natural rubber or styrene/butadiene rubber, high styrene resin, butyl rubber, ethylene/propylene rubbers, neoprene rubber, nitrile rubber, cis-1,4-polyisoprene rubber, silicone rubber, chlorosulfonated rubber, polyethylene rubber, epichlorohydrin rubber, fluorocarbon rubber, fluorosilicone rubber, polyurethane rubber, polyacrylic rubber and polysulfide rubber.

[0018] Of the various latexes which can be utilized, those prepared by emulsion polymerization processes are preferred. A particularly preferred latex for use in accordance with this invention is a styrene/butadiene copolymer latex emulsion prepared by emulsion polymerization. The aqueous phase of the emulsion is an aqueous colloidal dispersion of the styrene/butadiene copolymer. The latex dispersion usually includes water in an amount in the range of from about 40% to about 70% by weight of the latex, and in addition to the dispersed styrene/butadiene particles, the latex often includes small quantities of an emulsifier, polymerization catalysts, chain modifying agents and the like. The weight ratio of styrene to butadiene in the latex can range from about 10%:90% to about 90%:10%.

[0019] It is understood that styrene/butadiene latexes are often commercially produced as terpolymer latexes which include up to about 3% by weight of a third monomer to assist in stabilizing the latex emulsions. The third monomer, when present, generally is anionic in character and includes a carboxylate, sulfate or sulfonate group. Other groups that may be present on the third monomer include phosphates, phosphonates or phenolics. Non-ionic groups which exhibit steric effects and which contain long ethoxylate or hydrocarbon tails can also be present.

[0020] A particularly suitable styrene/butadiene aqueous latex has a styrene/butadiene weight ratio of about 25%:

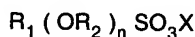
75%, and the styrene/butadiene copolymer is suspended in a 50% by weight aqueous emulsion. This styrene/butadiene aqueous latex in combination with the other components of the cement compositions of this invention provides excellent resiliency to a set cement composition without the appreciable loss of bond strength in the set cement. A latex of this type is available from Halliburton Energy Services of Duncan, Oklahoma under the trade designation "LATEX 2000".

" The aqueous latex used is included in the cement compositions of this invention in an amount in the range of from about 2.5% to about 45% by weight of the hydraulic cement in the composition (from about 0.94 to about 19 dm³/sack (0.25 to about 5.0 gal/sack)), more preferably from about 4.5% to about 22% (from about 1.9 to about 9.5 dm³/sack (0.5 to about 2.5 gal/sack)) and most preferably about 9% (about 3.8 dm³/sack (1 gal/sack)).

[0021] In order to prevent the aqueous latex from prematurely coagulating and increasing the viscosity of the cement composition, an effective amount of a latex stabilizer is included in the cement composition. Latex stabilizers are comprised of one or more surfactants which function to prevent latex coagulation. Those which are particularly suitable for use in accordance with the present invention are surfactants having the formula



wherein R is an alkyl group having from about 5 to about 30 carbon atoms, Ph is phenyl and m is an integer in the range of from about 5 to about 50, and surfactants of the general formula



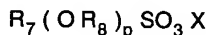
wherein R₁ is selected from the group consisting of alkyl groups having from 1 to about 30 carbon atoms, cycloalkyl groups having 5 or 6 carbon atoms, C₁ - C₄ alkyl substituted cycloalkyl groups, phenyl, alkyl substituted phenyl of the general formula (R₃)_aPh-wherein Ph is phenyl, R₃ is an alkyl group having from 1 to about 18 carbon atoms and a is an integer of from 1 to 3, and phenyl-alkyl groups wherein the alkyl groups have from 1 to about 18 carbon atoms and the phenyl-alkyl groups have a total of from about 8 to about 28 carbon atoms, R₂ is a substituted ethylene group of the formula -CH₂CH₂R₄ wherein R₄ is selected from hydrogen, methyl, ethyl or mixtures thereof, and n is a number from 0 to about 40 provided that when R₁ is phenyl or alkyl substituted phenyl n is at least one, and X is any compatible cation. A preferred surfactant in this group is ethoxylated nonylphenyl containing in the range of from about 20 to about 30 moles of ethylene oxide.

[0022] Another preferred surfactant in the group is a sodium salt having the general formula

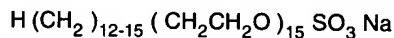


wherein R₅ is an alkyl group having in the range of from 1 to about 9 carbon atoms, R₆ is the group -CH₂CH₂-, o is an integer from about 10 to about 20 and X is a compatible cation.

[0023] Yet another preferred surfactant in the group is a sodium salt having the formula



wherein R₇ is an alkyl group having in the range of from about 5 to about 20 carbon atoms, R₈ is the group -CH₂CH₂-, p is an integer in the range of from about 10 to about 40 and X is a compatible cation. A particularly preferred surfactant of this type is the sodium salt of a sulfonated compound derived by reacting a C₁₂ to C₁₅ alcohol with about 15 moles of ethylene oxide having the formula



which is commercially available under the name "AVANEL S150™" from PPG Mazer, Mazer Chemicals, a Division of PPG Industries, Inc., 3938 Porett Drive, Gurnee, Illinois 60031.

[0024] Of the various latex stabilizers described above which can be used, ethoxylated nonylphenol containing in the range of from about 15 to about 40 moles of ethylene oxide and "AVANEL S150™", i.e., the sodium salt of a sulfonated and ethoxylated compound having the formula H (CH₂)₁₂₋₁₅ (CH₂CH₂O)₁₅ SO₃ Na are preferred, with H (CH₂)₁₂₋₁₅ (CH₂CH₂O)₁₅ SO₃ Na being the most preferred.

[0025] While different amounts of latex stabilizer are included in the cement composition depending on the particular

aqueous rubber latex used, the latex stabilizer is usually included in the cement composition in an amount in the range of from about 9% to about 35% by weight of the aqueous rubber latex included therein (from about 0,08 to about 6,6 dm³/sack (0.02 to about 1.75 gal/sack) of cement). When the aqueous latex is an aqueous styrene/butadiene latex, the latex stabilizer utilized is preferably included in the cement composition in an amount in the range of from about 9% to about 35% by weight of the aqueous rubber latex included in the composition (from about 0,08 to about 6,6 dm³/sack (0.02 to about 1.75 gal/sack) of cement), more preferably from about 15% to about 25% (from about 0,15 to about 4,7 dm³/sack (0.04 to about 1.25 gal/sack)) and most preferably about 20% (about 0,8 dm³/sack (0.2 gal/sack)).

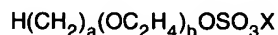
[0026] While the water in the aqueous rubber latex used in forming the cement compositions of this invention can be adequate for producing a pumpable slurry and hydrating the cementitious materials therein, additional water can be added to the composition as required for pumpability. The water can be from any source provided it does not contain in excess of compounds that adversely affect other components in the cement composition. For example, the water can contain various salts such as sodium, potassium and calcium chloride or the like. Generally, water is present in a cement slurry composition of this invention in an amount in the range of from about 22% to about 95% by weight of hydraulic cement therein (from about 9,5 to about 40 dm³/sack (2.5 to about 10.7 gal/sack)).

[0027] A light weight, foamed, highly resilient well cement composition of this invention is comprised of a hydraulic cement of the type described above, an aqueous rubber latex of the type described above present in an amount in the range of from about 2.5% to about 45% by weight of hydraulic cement in the composition (from about 0,95 to about 19 dm³/sack (0.25 to about 5.0 gal/sack)), an effective amount of a latex stabilizer of the type described above, an effective amount of a defoaming agent, a compressible gas present in an amount sufficient to foam the composition and produce a density in the range of from about 8 pounds per gallon to about 16 pounds per gallon, an effective amount of a foaming agent and an effective amount of a foam stabilizer.

[0028] The defoaming agent prevents foaming during mixing of the cement composition prior to foaming the composition. That is, because the aqueous rubber latex includes surfactants for emulsifying the latex and latex stabilizer which also function as foaming agents, a large bubble, unstable foam is produced when the hydraulic cement and silica are mixed with the latex. The defoaming agent prevents the formation of the large bubble foam so that a small bubble stable foam can be subsequently formed. The defoaming agent can comprise any of the compounds well known for such capabilities such as the polyol silicon compounds: A preferred such defoaming agent is polydimethylsiloxane which is commercially available from Halliburton Energy Services of Duncan, Oklahoma, under the trade designation "D-AIR™." The defoaming agent is generally included in the cement composition in an amount in the range of from about 0.1% to about 0.9% by weight of the hydraulic cement therein (from about 0,04 to about 0,4 dm³/sack (0.01 to about 0.1 gal/sack)), more preferably from about 0.18% to about 0.7% (from about 0,08 to about 0,3 dm³/sack (0.02 to about 0.08 gal/sack)) and most preferably about 0.18% (about 0,8 dm³/sack (0.02 gal/sack)).

[0029] The compressible gas functions to foam the cement composition, to prevent pressurized formation fluid influx into the cement composition when setting and contributes to the resiliency of the set composition. The gas is preferably nitrogen or air, with nitrogen being the most preferred. Generally, the gas is present in an amount sufficient to foam the cement slurry and produce a slurry density in the range of from about 8 to about 16 pounds per gallon, more preferably from about 12 to about 15 pounds per gallon and most preferably about 13 pounds per gallon. The amount of gas which is present in a foamed cement composition of this invention generally ranges from about 8.5% to about 50% by volume of the resulting foamed cement composition.

[0030] In order to facilitate foaming and to stabilize the foamed slurry, a foaming agent is included in the cement composition. Suitable foaming agents are surfactants having the general formula:



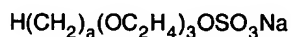
wherein:

a is an integer in the range of from about 5 to about 15;

b is an integer in the range of from about 1 to about 10; and

X is any compatible cation.

A particularly preferred foaming agent is a surfactant of the above type having the formula:

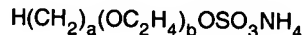


wherein:

a is an integer in the range of from about 6 to about 10. This surfactant is commercially available from Halliburton

Energy Services of Duncan, Oklahoma, under the trade designation "CFA-S™."

[0031] Another particularly preferred foaming agent of the above mentioned type is a surfactant having the formula:



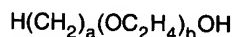
wherein:

a is an integer in the range of from about 5 to about 15; and

b is an integer in the range of from about 1 to about 10.

This surfactant is available from Halliburton Energy Services under the trade name "HALLIBURTON FOAM ADDITIVE™."

[0032] Another foaming agent which can be utilized in the cement compositions of this invention includes polyethoxylated alcohols having the formula:



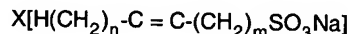
wherein:

a is an integer in the range of from about 10 to about 18; and

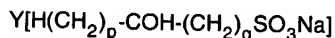
b is an integer in the range of from about 6 to about 15.

This surfactant is available from Halliburton Energy Services under the trade name "AQF-1™."

[0033] Yet another foaming agent which can be used is a sodium salt of alpha-olefinic sulfonic acid (AOS) which is a mixture of compounds of the formulas:



and



wherein:

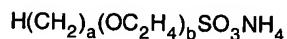
n and m are individually integers in the range of from about 6 to about 16;

p and q are individually integers in the range of from about 7 to about 17; and

X and Y are fractions with the sum of X and Y being 1.

This foaming agent is available from Halliburton Energy Services under the trade name "AQF-2™."

[0034] Still another foaming surfactant which can be used is an alcohol ether sulfate of the formula:



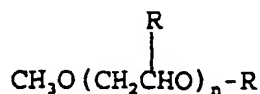
wherein:

a is an integer in the range of from about 6 to about 10; and

b is an integer in the range of from about 3 to about 10.

[0035] The particular foaming agent employed will depend on various factors such as the types of formations in which the foamed cement is to be placed. Generally, the foaming agent utilized is included in a cement composition of this invention in an amount in the range of from about 1.5% to about 10% by weight of water in the composition. When the foaming agent is one of the preferred surfactants described above, it is included in the composition in an amount in the range of from about 4% to about 9.5% by weight of water therein.

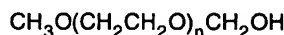
[0036] A foam stabilizer is also included in the foamed cement composition to enhance the stability of the foamed cement slurry. One such foam stabilizing agent is a compound of the formula:



wherein:

R is hydrogen or a methyl radical; and
n is an integer in the range of from about 20 to about 200.

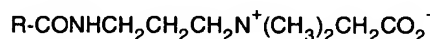
A particularly preferred foam stabilizing agent of the above type is a methoxypolyethylene glycol of the formula:



wherein:

n is in the range of from about 100 to about 150. This foam stabilizing agent is commercially available from Halliburton Energy Services under the trade designation "HALLIBURTON FOAM STABILIZER™."

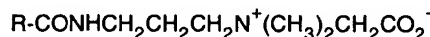
[0037] The preferred foam stabilizing agent is a compound having the formula:



wherein:

R is a C₁₀ to C₁₈ saturated aliphatic hydrocarbon group or an oleyl group or a linoleyl group.

A particularly preferred stabilizing agent of the above type is an amidopropylbetaine of the formula:



wherein:

R is a cocoyl group.

This foam stabilizing agent is commercially available from Halliburton Energy Services under the trade designation "HC-2™."

[0038] The foam stabilizer is included in a cement composition of this invention in an amount in the range of from about 0.75% to about 5% by weight of water utilized. When the foam stabilizing agent is one of the particularly preferred agents described above, it is preferably present in the composition in an amount in the range of from about 2% to about 5% by weight of water.

[0039] Another foamed well cement composition of this invention is comprised of a hydraulic cement of the type described above, an aqueous rubber latex described above present in an amount in the range of from about 2.5% to about 45% by weight of hydraulic cement in the composition (from about 0.95 to about 19 dm³/sack (0.25 to about 5 gal/sack)), an effective amount of a latex stabilizer described above, an effective amount of a defoaming agent described above, a compressible gas described above present in an amount sufficient to foam the cement composition and produce a cement composition density in the range of from about 0.96 kg/dm³ (8 pounds per U.S. gallon) to about 1.91 kg/dm³ (16 pounds per U.S. gallon), an effective amount of a foaming agent described above and an effective amount of a foam stabilizer described above.

[0040] This foamed cement composition which is preferred in some applications is light weight, resilient and resists pressurized formation fluid migration.

[0041] The well cement compositions useful herein can include other additives which are well known to those skilled in the art including fluid loss control additives, set retarding additives, dispersing agents, formation conditioning additives, set accelerators and the like.

[0042] Dispersing agents can be utilized to facilitate the use of lower quantities of water and to promote higher set content cement strength. A particularly suitable dispersing agent for use with the well cement compositions of this invention is comprised of the condensation polymer product of an aliphatic ketone, an aliphatic aldehyde and a com-

pound which introduces acid groups into the polymer, e.g., sodium sulfite. Such a dispersant is described in U.S. Patent No. 4,557,763 issued to George et al. on December 10, 1985.

[0043] Examples of fluid loss control additives are cellulose derivatives such as carboxymethylhydroxyethylcellulose, hydroxyethylcellulose, modified polysaccharides, polyacrylamides, guar gum derivatives, 2-acrylamido-2-methylpropane sulfonic acid copolymers, polyethyleneamine and the like.

[0044] Set retarding additives are included in the cement compositions when it is necessary to extend the time in which the cement composition can be pumped so that it will not thicken or set prior to being placed at a desired location in the well being cemented. Examples of set retarders which can be used include lignosulfonates such as calcium and sodium lignosulfonate, organic acids such as tartaric acid and gluconic acid, copolymers and others. The proper amount of retarder required for particular conditions can be determined by conducting a "thickening time test" for the particular retarder and cement composition. Such tests are described in the API Specification For Materials and Testing for Well Cements, API Specification 10 mentioned above.

[0045] A particularly preferred set retarder for use in accordance with the present invention is a copolymer or copolymer salt of 2-acrylamido-2-methylpropanesulfonic acid and acrylic acid. The copolymer comprises from about 40 to about 60 mole percent 2-acrylamido-2-methylpropanesulfonic acid with the balance comprising acrylic acid, and the copolymer or salt preferably has an average molecular weight below about 5,000. This copolymer set retarder is preferably utilized in the composition when the bottom hole circulating temperature exceeds about 200°F. The retarder has been found to both retard the setting of the cement at elevated formation temperatures and to stabilize the aqueous styrene/butadiene latex against agglomeration or inversion at the elevated temperature. The set retarder is generally added to the cement composition in an amount in the range of from about 0.1% to about 6% by weight of hydraulic cement in the composition.

[0046] The cement compositions of this invention may be prepared in accordance with any of the well known mixing techniques so long as the latex and latex stabilizing surfactant are not directly admixed without prior dilution by other liquids present. In one preferred method, a quantity of water is introduced into a cement blender and defoamer, latex and latex stabilizer are then sequentially added with suitable agitation to disperse the constituents. Any other liquid additives may then be admixed with the slurry followed by the hydraulic cement, and other dry solids. The mixture is agitated for a sufficient period of time to admix the components and form a pumpable non-foamed slurry. When the slurry is foamed, it is pumped to the well bore and the foaming agent and foam stabilizer followed by the gas are injected into the slurry on the fly. As the slurry and gas flow through the well bore to the location where the resulting foamed cement composition is to be placed, the cement composition is foamed and stabilized.

[0047] The methods of this invention for cementing a zone in a well basically comprise the steps of placing a cement composition of this invention which sets into a highly resilient, high bond strength, substantially impermeable mass in the subterranean zone to be cemented, and maintaining the cement composition in the zone for a time sufficient for the cement composition to set therein.

[0048] In order to further illustrate the improved cement compositions and methods of this invention, the following examples are given.

Example 1

[0049] Test samples of foamed cement compositions of this invention comprised of hydraulic cement, fumed silica, an aqueous rubber latex, a latex stabilizer, a defoaming agent, air, a foaming agent and a foam stabilizer were prepared. One of the foamed cement compositions also included hemitite weighting material, 100 mesh sand, a set retarder and a retarder intensifier. For each test sample, an unfoamed cement slurry including the defoaming agent was first prepared utilizing a mixing device. A predetermined amount of the resulting slurry was then placed in a fixed volume blender jar having a stacked blade assembly. The foaming agent and foam stabilizer were then added to the jar and the contents were mixed at high speed. The high speed mixing by the stacked blade assembly caused the slurry to be foamed with air. Descriptions of the test samples are set forth in Table IA below.

[0050] The foamed test samples were allowed to set for 1 week at 140°F and atmospheric pressure after which portions of the test samples were subjected to various tests to determine their properties. More specifically, unconfined uniaxial and confined triaxial strength tests were conducted and Young's Moduli and Poisson's Ratios were determined as well as bulk compressibilities, shear moduli and tensile strengths, all in accordance with the standardized tests and procedures of the American Society for Testing and Materials (ASTM) set forth, for example, in ASTM Section D 1456. The results of the tests and determinations are set forth in Table IB below.

TABLE IA
Foamed Cement Compositions

		(11) Cement Composition Components													
Sample No.	Hydraulic Cement	Fumed Silica, % by Weight of Cement, or gal per 94 lb Sack of Cement	Aqueous Rubber Latex, gal per 94 lb Sack of Cement	Latex Stabilizer ¹ , gal per 94 lb Sack of Cement	Hemite ² , % by Weight of Cement	Fluid Loss Control Agent ³ , % by Weight of Cement	Sand (100 Mesh), % by Weight of Cement	Set Retarder ⁴ , % by Weight of Cement	Set Retarder Intensifier ⁵ , % by Weight of Cement	Defoaming Agent ⁶ , gal per 94 lb Sack of Cement	Foaming Agent ⁷ , % by Weight of Water	Foam Stabilizer ⁸ , % by Weight of Water	Water, gal per 94 lb Sack of Cement	Foamed Density, lb/gal	
1	Portland Class II	10%	1	0.2	-	-	-	-	-	0.02	7.5	3.75	5.41	15	13.6
2	Portland Class II	10%	2	0.2	-	-	-	-	-	0.02	9.4	4.7	4.32	15	13.6
3	Portland Class II	1.63 gal/sk ⁹	1	0.3 ¹⁰	200	0.5	40	3.3	2.4	0.02	4.5	2.3	5.01	22	17

¹ Aqueous styrene/butadiene (25%:75% by wt.) latex containing 50% by weight water ("LATEX 2000" from Halliburton Energy Services).

² Sodium salt of a sulfonated and ethoxylated compound having the formula $H(C_6H_4)_2SO_3Na$ ("AVANEL S150" from PPG Mazer).

³ Copolymer of "AMPS" and N,N-dimethylacrylamide (U.S. Patent No. 4,555,269).

⁴ Copolymer of "AMPS" and acrylic acid (U.S. Patent No. 4,941,536).

⁵ Tartaric acid.

⁶ Polydimethylsiloxane.

⁷ Sodium salt of alpha-olefinic sulfonic acid.

⁸ Cocoylamidopropylbetaine.

⁹ Aqueous dispersion of 50% fumed silica by weight of water.

¹⁰ Ethoxylated nonylphenol with 15-40 moles of ethylene oxide substituted for latex stabilizer described in footnote 2.

(11) gal (US) = 3.79 dm³

(12) lb/gal = 0.1198 kg/dm³

TABLE IB
Bond Strength And Resiliency Test Results

Sample No.	(4) Shear Bond Strength, psi	Hydraulic Bond Strength, psi	Confined Triaxial												Failure Envelope Friction Angle, Degrees			
			Unconfined Uniaxial		Young's Modulus (EX)(10 ⁴)						Poisson's Ratio		Plastic Failure, psi			Bulk Compressibility at 1000 psi, 10 ¹ psi	Shear Modulus at 1000 psi, 10 ¹ psi	Tensile Strength (Briquet), psi
			Young's Modulus (EX)(10 ⁴)	Poisson's Ratio	Compressive Strength, psi		Confining Pressure, psi		Confining Pressure, psi		psi							
					500	2000	500	2000	500	2000								
1	163(13.8) ¹	630	-	-	1388 ²	0.048	0.312	0.091	0.158	0.1494	0.079	2900	4200	4000	0.94	13.57	194 ³	31.5
2	154(13.85) ¹	720	-	-	1460 ²	0.076	0.304	0.026	0.090	0.2883	0.065	2255	3200	3100	0.418	11.8	250 ³	19.5
3	-	-	0.35	0.107	2700 ³	0.26	0.3	0.282	0.086	0.144	0.109	3850	4925	6950	6.2	-	-	22

¹ The number in parentheses is the test sample density in lb/gal.

² The base pressure was 2220 psi.

³ The base pressure was 286 psi.

⁴ 1 psi = 6.895 kPa

[0051] From the results set forth in Table IB, it can be seen that the foamed cement compositions of this invention have excellent bond strengths and resiliencies.

Example 2

[0052] Test samples of foamed cement compositions of this invention comprised of API Portland Class G hydraulic cement, an aqueous rubber latex, a latex stabilizer, a fluid loss control agent, a set accelerator, a defoaming agent, air, a foaming agent, and a foam stabilizer were prepared. For each test sample, a base unfoamed cement slurry including the defoaming agent was first prepared followed by foaming of the base slurry with a foaming agent and foam stabilizer as described in Example 1 above.

[0053] The various strength tests and modulus and ratio determinations described in Example 1 were conducted and determined.

[0054] The descriptions of the test samples are set forth in Table IIA below and the results of the tests and determinations are set forth in Table IIB below.

TABLE IIA
Foamed Cement Compositions

Sample No.	Hydraulic Cement	(9)		(10)					Cement Composition Components					(11)	
		Sand (100 mesh), % by Weight of Cement	Aqueous Rubber Latex ¹ gal per 94 lb Sack of Cement	Latex Stabilizer ² , gal per 94 lb Sack of Cement	Fluid Loss Control Agent ³ , % by Weight of Cement	Biopolymer ⁴ , % by Weight of Cement	Accelerator ⁵ , % by Weight of Cement	Defoaming Agent ⁶ , gal per 94 lb Sack of Cement	Foaming Agent ⁷ , % by Weight of Water	Foam Stabilizer ⁸ , % by Weight of Water	Water, gal per 94 lb Sack of Cement	Density of Base Slurry, lb/gal	Foamed Density lb/gal		
1	Portland Class G	100	1	0.3	0.2	0.14	4	0.02	4.3	2.2	6.28	16.3	14		
2	Portland Class G	100	1	0.3	0.2	0.14	4	0.02	4.3	2.2	6.28	16.3	12		
3	Portland Class G	100	2	0.3	0.2	0.22	4	0.02	5.1	2.6	5.28	16.3	14		
4	Portland Class G	100	2	0.3	0.2	0.22	4	0.02	5.1	2.6	5.28	16.3	12		
5	Portland Class G	-	5	0.3	0.5	-	2	0.02	5.2	2.6	3.33	17.5	15		

¹ Aqueous styrene/butadiene (25%:75% by wt.) latex containing 50% by weight water ("LATEX 2000" from Halliburton Energy Services).

² Sodium salt of a sulfonated and ethoxylated compound having the formula $H(CH_2)_{12-14}(CH_2CH_2O)_nSO_3Na$ ("AVANEL S150" from PPG Mazer).

³ Copolymer of "AMPS" and N,N-dimethylacrylamide (U.S. Patent No. 4,555,269).

⁴ Welan gum.

⁵ Calcium chloride.

⁶ Polydimethylsiloxane.

⁷ Sodium salt of alpha-olefinic sulfonic acid.

⁸ Cocoylamidopropylbetaine.

⁽⁹⁾ 100 mesh = 0.149 mm

⁽¹⁰⁾ 1 gal (US) = 3.79 dm³

⁽¹¹⁾ 1 lb/gal = 0.1198 kg/dm³

TABLE IIB
Bond Strength And Resiliency Test Results

Sample No.	(4) Shear Bond Strength, psi	Hydraulic Bond Strength, psi	Confined Triaxial												Bulk Compressibility at 1000 psi, 10 ³ psi	Shear Modulus at 1000 psi, 10 ⁴ psi	Tensile Strength (Briquet), psi	Failure Envelope Friction Angle, Degrees	
			Unconfined Uniaxial		Young's Modulus (EX10 ⁴)		Poisson's Ratio		Plastic Failure, psi										
			Young's Modulus (EX10 ⁴)	Poissons Ratio	Compressive Strength, psi	Confining Pressure, psi		Confining Pressure, psi											
						500	1000	2000	500	1000	2000								
1	303	780	-	-	-	-	0.039	-	-	0.1187	-	-	3220	-	5.86	1.745	-		
2	244(12.1) ¹	660	-	-	-	-	0.029	-	-	0.0436	-	-	2000	-	9.44	1.389	-		
3	322(14.1) ¹	775	-	-	-	-	0.048	-	-	0.1478	-	-	3700	-	4.4	2.09	-		
4	287(12.2) ¹	660	-	-	-	-	0.0353	-	-	0.1808	-	-	2200	-	5.47	1.482	-		
5	86(15.4) ¹	700	0.0025	0.102	392 ²	0.013	0.013	0.013	0.025	0.078	0.128	0.171	1948	3096	4857	17.169	0.576	232 ³	9

¹ The number in parentheses is the test sample density in lb/gal.

² The base pressure was 2220 psi.

³ The base pressure was 280 psi.

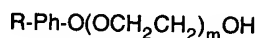
⁴ 1 psi = 6.895 kPa

[0055] From the results set forth in Table IIB, it can be seen that the additional foamed cement compositions of this invention also have excellent bond strengths and resiliencies.

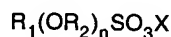
5 Claims

1. A well cement composition having improved mechanical properties including elasticity and ductility, the composition comprising a hydraulic cement; an aqueous rubber latex present in an amount of from 2.5% to 45% by weight of hydraulic cement in said composition; a latex stabilizer; a defoaming agent comprised of polydimethylsiloxane present in an amount of from 0.1% to 0.9% by weight of cement in said composition; a gas present in an amount sufficient to foam said cement composition and produce a cement composition density in the range of from 0,96 to 1,91 kg/dm³ (8 to 16 pounds per U.S. gallon); a foaming agent; and a foam stabilizer.

2. A composition according to claim 1, wherein the latex stabilizer is selected from surfactants having the formula



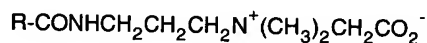
wherein R is an alkyl group having from 5 to 30 carbon atoms, Ph is phenyl and m is an integer of from 5 to 50, and surfactants of the general formula



wherein R₁ is selected from alkyl groups having from 1 to 30 carbon atoms, cycloalkyl groups having 5 or 6 carbon atoms, C₁ - C₄ alkyl substituted cycloalkyl groups, phenyl, alkyl substituted phenyl of the general formula (R₃)_aPh- wherein Ph is phenyl and R₃ is an alkyl group having from 1 to 18 carbon atoms and a is an integer of from 1 to 3, and phenyl-alkyl groups wherein the alkyl groups have from 1 to 18 carbon atoms and the phenyl-alkyl groups have a total of from 8 to 28 carbon atoms, R₂ is a substituted ethylene group of the formula -CH₂CH₂R₄ wherein R₄ is hydrogen, methyl, ethyl or any mixture thereof, and n is a number from 0 to 40 provided that when R₁ is phenyl or alkyl substituted phenyl, n is at least one, and X is any compatible cation.

3. A composition according to claim 1 or 2, wherein the foaming agent is comprised of the sodium salt of alpha-olefinic sulfonic acid and is present in an amount of from 4% to 9.5% by weight of water in said composition.

4. A composition according to claim 1, 2 or 3, wherein the foam stabilizer is comprised of an amidopropylbetaine of the formula:



wherein R is a cocoyl group, the foam stabilizer being present in an amount of from 2% to 5% by weight of water in said composition.

5. A composition according to claim 1, 2, 3 or 4, wherein water is present in said composition in an amount of from 22% to 95% by weight of cement therein.

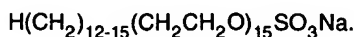
6. A composition according to any of claims 1 to 5, wherein said hydraulic cement is Portland cement, and/or said aqueous rubber latex is an aqueous styrene/butadiene latex.

7. A composition according to claim 6, wherein an aqueous styrene/butadiene latex is present which contains water in an amount of substantially 50% by weight of said latex, and the weight ratio of styrene to butadiene in said latex is substantially 25%:75%.

8. A composition according to claim 6 or 7, wherein a latex stabilizer is present in said cement composition in an amount of from 9% to 35% by weight of the aqueous styrene/butadiene latex therein.

9. A composition according to claim 8, wherein the latex stabilizer is selected from nonylphenol ethoxylated with from

15 to 40 moles of ethylene oxide and the sodium salt of a sulfonated and ethoxylated compound having the formula



10. A method of cementing in a subterranean well, which comprises introducing a cement composition as claimed in any of claims 1 to 9, and allowing said cement composition to set in said well.

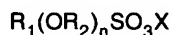
Patentansprüche

1. Eine Bohrloch-Zementierzusammensetzung mit verbesserter mechanischer Wirkung, einschließlich Elastizität und Dehnbarkeit, die sich aus einem hydraulischen Zement, einem in 2,5 bis 45 % Massenanteil des hydraulischen Zements vorhandenen wässrigen Gummilatex, einem in zum Schäumen der Zementzusammensetzung ausreichender Menge vorhandenem Gas, um eine Zementzusammensetzungs-Dichte im Bereich von 0,96 bis 1,91 kg/dm³ herbeizuführen, einem Schaummittel und einem Schaumstabilisator zusammensetzt.

2. Eine Zusammensetzung nach Anspruch 1, bei der der Latexstabilisator aus Tensiden mit der folgenden Formel ausgewählt wird:



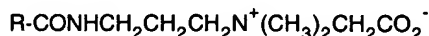
wobei R eine Alkylgruppe mit zwischen 5 bis 30 Kohlenatomen, Ph ein Phenyl und m eine Ganzzahl von 5 bis 50 ist und die Tensiden der allgemeinen folgenden Formel entsprechen:



wobei R₁ aus Alkylgruppen mit zwischen 1 bis 30 Kohlenatomen, Cycloalkangruppen mit 5 oder 6 Kohlenatomen, C₁-C₄ alkylsubstituierten Cycloalkangruppen, Phenyl, alkylsubstituiertes Phenyl mit der allgemeinen Formel (R₃)_a Ph-, wobei Ph Phenyl und R₃ eine Alkylgruppe mit zwischen 1 und 18 Kohlenatomen und a eine Ganzzahl zwischen 1 und 3 ist, und Phenyl-Alkylgruppen ausgewählt wird, wobei die Alkylgruppen zwischen 1 und 18 Kohlenatome und die Phenyl-Alkyl insgesamt zwischen 8 und 28 Kohlenatomen aufweisen, R₂ eine substituierte Ethylgruppe mit der Formel -CH₂CH₂R₄ darstellt, wobei R₄ Wasserstoff, Ethyl oder eine Mischung beider darstellt und n eine Zahl zwischen 0 und 40 ist, vorausgesetzt R₁ ist Phenyl oder alkylsubstituiertes Phenyl, n ist mindestens eins und X ist ein verträgliches Kation.

3. Eine Zusammensetzung nach Ansprüchen 1 oder 2, wobei sich das Schaummittel aus dem Natriumsalz alphaolefinischer Sulfosäure zusammensetzt und in Mengen zwischen 4 und 9,5 % Massenanteil des Wassers in der Zusammensetzung vorhanden ist.

4. Eine Zusammensetzung nach einem der Ansprüche 1, 2 oder 3, wobei der Schaumstabilisator aus einem Amidopropylbetain mit folgender Formel besteht:



wobei R eine Cocoylgruppe darstellt und der Schaumstabilisator in Mengen zwischen 2 und 5 % Massenanteil des Wassers der Zusammensetzung vorhanden ist.

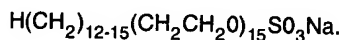
5. Eine Zusammensetzung nach Ansprüchen 1, 2, 3 oder 4, wobei Wasser in Mengen von 22 bis 95 % Massenanteil des Zements in der Zusammensetzung vorhanden ist.

6. Eine Zusammensetzung nach Ansprüchen 1 bis 5, wobei der erwähnte hydraulische Zement Portlandzement ist und/oder der erwähnte Latex ein wässriger Styrol-/Butadienlatex ist.

7. Eine Zusammensetzung nach Anspruch 6, bei der ein wässriger Styrol/Butadienlatex vorhanden ist, der Wasser

in einer Menge von wesentlich 50 % Massenanteil des erwähnten Latex enthält, und das Gewichtsverhältnis zwischen Styrol und Butadien im erwähnten Latex wesentlich bei 25:75 % liegt.

8. Eine Zusammensetzung nach Ansprüchen 6 oder 7, bei der ein Latexstabilisator in der erwähnten Zementzusammensetzung in einer Menge von 9 bis 35% Massenanteil des darin befindlichen wässrigen Styrol-/Butadienlatex vorhanden ist.
9. Eine Zusammensetzung nach Anspruch 8, bei der der Latexstabilisator aus mit 15 bis 40 Mol Ethylenoxid ethoxyliertem Nonylphenol und dem Natriumsalz einer sulfonierten und ethoxylierten Zusammensetzung mit der folgenden Formel besteht:



10. Eine Vorgehensweise der Zementierung eines unterirdischen Bohrlochs, bestehend aus dem Einführen einer Zementzusammensetzung nach einem der Ansprüche 1 bis 9 und dem Zulassen der Verfestigung der erwähnten Zementzusammensetzung im erwähnten Bohrloch.

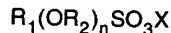
Revendications

1. Une composition de ciment pour puits ayant des propriétés mécaniques améliorées, y compris l'élasticité et la ductilité, la composition comprenant un ciment hydraulique ; un latex de caoutchouc aqueux présent en une quantité de 2,5% à 45% en poids du ciment hydraulique dans ladite composition ; un stabilisateur de latex ; un agent désémulsifiant composé de polydiméthylsiloxane présent en une quantité de 0,1% à 0,9 en poids du ciment de ladite composition ; un gaz présent en une quantité suffisante pour faire mousser ladite composition et produire une densité de composition de ciment dans la plage de 0,96 à 1,31 kg/dm³ (8 à 16 pounds par gallon U.S.) ; un agent moussant ; et un stabilisateur de mousse.

2. Une composition selon la revendication 1, dans laquelle le stabilisateur de latex est sélectionné parmi des surfactants ayant la formule

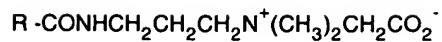


dans laquelle R est un groupe alkyle ayant de 5 à 30 atomes de carbone, Ph est phényle et m est un nombre entier de 5 à 50, et des surfactants ayant la formule générale



dans laquelle R₁ est sélectionné parmi des groupes alkyles ayant de 1 à 30 atomes de carbone, des groupes cycloalkyles ayant 5 ou 6 atomes de carbone, des groupes cycloalkyles à substitution alkyle C₁ - C₄, des phényles, des phényles à substitution alkyle de la formule générale (R₃)_aPh- dans laquelle Ph est phényle et R₃ est un groupe alkyle ayant de 1 à 18 atomes de carbone, et a est un nombre entier de 1 à 3, et des groupes phénylalkyles, dans lesquels les groupes alkyles ont de 1 à 18 atomes de carbone et les groupes phénylalkyles ont de 1 à 18 atomes de carbone et les groupes phénylalkyles ont un total de 8 à 28 atomes de carbone, R₂ est un groupe éthylène substitué ayant la formule -CH₂CH₂R₄ dans laquelle R₄ est hydrogène, méthyle, éthyle ou un quelconque mélange de ceux-ci, et n est un nombre de 0 à 40 à condition que, lorsque R₁ est phényle ou phényle à substitution alkyle, n est au moins 1 et X est un quelconque cation compatible.

3. Une composition selon la revendication 1 ou 2, dans laquelle l'agent moussant comprend le sel de sodium de l'acide sulfonique alpha-oléfin et est présent en une quantité de 4 à 9,5% en poids de l'eau dans ladite composition.
4. Une composition selon la revendication 1, 2 ou 3, dans laquelle le stabilisateur de mousse se compose d'une amidopropylbétaine ayant la formule :



dans laquelle R est un groupe cocoyle, le stabilisateur de mousse étant présent en une quantité de 2% à 5 en poids de l'eau dans ladite composition.

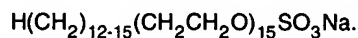
5 5. Une composition selon la revendication 1, 2, 3 ou 4, dans laquelle l'eau est présente dans ladite composition en une quantité de 22% à 95% en poids du ciment dans la composition.

10 6. Une composition selon l'une quelconque des revendications 1 à 5, dans laquelle ledit ciment hydraulique est un ciment Portland et/ou ledit latex de caoutchouc aqueux est un latex de styrène/butadiène aqueux.

15 7. Une composition selon la revendication 6, dans laquelle est présent un latex de styrène/butadiène aqueux qui contient de l'eau en une quantité sensiblement égale à 50% en poids dudit latex, et le rapport en poids du styrène au butadiène dans ledit latex égale sensiblement 25%:75%.

20 8. Une composition selon la revendication 6 ou 7, dans laquelle un stabilisateur de latex est présent dans ladite composition de ciment en une quantité de 9% à 35% en poids du latex au styrène/butadiène aqueux dans la composition.

9. Une composition selon la revendication 8, dans laquelle le stabilisateur de latex est sélectionné parmi un nonyl-phénol éthoxylé ayant de 15 à 40 moles d'oxyde d'éthylène et le sel de sodium d'un composé sulfoné et éthoxylé ayant la formule



30 10. Un procédé de cimentation dans un puits souterrain, qui comprend l'introduction d'une composition de ciment selon l'une quelconque des revendications 1 à 9, en laissant ladite composition de ciment durcir dans ledit puits.

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